(12) UK Patent Application (19) GB (11) 2 234 601 (13) A

(43) Date of A publication 06.02.1991

(21) Application No 8914425.7

(22) Date of filing 23.06.1989

(51) INT CL[5]
B41M 5/26

(52) UK CL (Edition K)
G2C CCXB

(56) Documents cited
EP 0190997 A2

(58) Field of search
UK CL (Edition J) G2C CCXB CHX
INT CL[4] B41M, G03C

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(54) Imaging method

(57) A method of forming images by imagewise exposing a sheet of a cellulosic substrate material impregnated with titanium dioxide to ultraviolet radiation produced by an excimer laser and having a wavelength of less than 400nm in order to cause the titanium dioxide present in the irradiated area(s) to darken, the said sheets of the cellulosic material being passed beneath the beam of the laser at a rate which correlates with the pulse rate of the laser.

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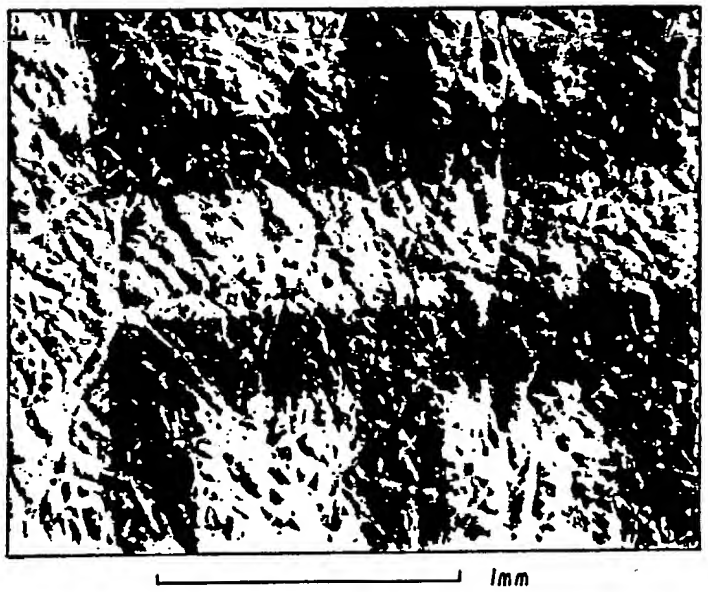
At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.



Photomicrograph of a sample of the exposed paper.

(Magnification factor x50)

PRINTING METHOD

The present invention relates to a method of printing onto a cellulosic substrate in which exposure with ultraviolet (UV) irradiation results in darkening of the exposed areas.

It is known that titanium dioxide (TiO_2) undergoes a colour change when exposed to ultraviolet irradiation. This colour change arises from the photo-induced reduction of titanium dioxide to give oxygen deficient titanium dioxide. The origin of the colour in oxygen defficient titanium dioxide is believed to be caused by either Ti^{3+} centres, small radius polarons of free electrons. The titanium dioxide colour change has been used to code titanium dioxide loaded plastic cables.

EP-A-0190997 discloses a process for marking high molecular organic materials containing at least one radiation-sensitive additive that undergoes a colour change when exposed to laser light. Titanium dioxide is a particular example of the radiation-sensitive additive.

We have now surprisingly found that there is no damage to cellulose fibres when a titanium dioxide loaded cellulosic substrate is subjected to exposure with ultraviolet radiation having a wavelength of less than 250nm, the only change being the conversion of the white TiO_2 to a black product.

It is surprising, in carrying out the method of the present invention, that there is no damage to the cellulosic fibres, the only interaction being the transformation of the white titanium dioxide to a black product.

Accordingly, the present invention provides a method of printing onto a cellulosic substrate which contains titanium dioxide, which method comprises

irradiating at least a part of the surface of the cellulosic substrate with ultraviolet radiation produced by a laser and having a wavelength of less than 400nm in order to cause the titanium dioxide present in the irradiated area(s) to darken.

In carrying out the method of the present invention the cellulosic substrate is subjected to exposure with ultraviolet radiation produced by a laser and having a wavelength of less than 400nm.

The ultraviolet radiation will is produced by a laser, because lasers provide easily controllable amounts of radiation. The radiation from lasers is usually highly monochromatic, well collimated, coherent and can be of high power. The fact that laser light is well collimated means that it is easy to direct and focus the light to one particular area. However, in some cases where it is desired to irradiate a more general area a broad-area beam may be used. A mask may then be employed to cover areas which are to be protected from exposure.

Some methods of ensuring selective absorption at a particular area rely on scanning the beam or defocussing/focussing the beam.

One particular type of laser which emits ultraviolet light is an excimer laser and this type of laser is preferred for use in the method of the present invention. Excimer lasers employ compounds known as excimers which have no stable ground state, but which may have excited states when temporarily bound to other molecules. Examples are lasers which employ mixtures of noble gases with halogens such as the krypton fluoride (KF) laser with output at 248 nm or the argon fluoride (ArF) laser with output at 193 nm. These lasers are generally used to produce pulsed output. The pulse durations are gen rally of th order of about 0 to 20 nanoseconds with a very

high peak power. Typically, the output of excimer lasers will be in the range of 50 to 100 watts. Preferably the cellulosic surface is irradiated with one or more pulses of ultraviolet radiation of an average density of $3J/cm^2$.

It is preferable to employ pulsed radiation of short duration such as that produced by excimer lasers in the process of the present invention. The pulsed ultraviolet radiation produced by excimer lasers is of short duration and penetrates only the surface layer of the cellulosic substrate. Thus the likelihood of heating of the area beside and beneath the area being exposed is reduced.

An article entitled Excimer Lasers by Poulin et al, P.C. Fab. June 1988, describes the nature of excimer lasers and discusses some of the applications that they are finding in the printed circuit industry.

The cellulosic substrate which is printed according to the method of the invention may be, for example, paper, card, cardboard, coated paper or a paper covered laminate material.

In carrying out the method of the present invention the cellulosic substrate may have the titanium dioxide pigment impregnated uniformly at least throughout its surface layers. Exposure of the cellulosic substrate through a mask will thus result in darkening of the titanium dioxide only in the exposed areas. Alternatively, the cellulosic substrate may have the titanium dioxide selectively impregnated therein and exposure of the whole of the substrate surface will darken the surface in the selectively impregnated areas only. Various specific applications of the method of the present invention are discussed below:

Security Printing

Since printing according to the method of the

invention extends into the thickness of the paper without affecting the cellulosic structure, it can not be erased by abrasion or altered without damaging the integrity of the matrix. This is a necessary requirement for security printing, such as legal documents, certificates, passports, cheques and bank notes.

Document Validation

Titanium dioxide may be selectively impregnated into paper forming a water-mark type of pattern. The paper is then validated by a single exposure which develops the latent image.

Origin Of Paper

The water-mark principle described above can be exploited with photocopier paper. The latent image identifies the photocopier when trying to trace where an illicit copy was made.

Selective Masking

Areas of a sheet that are for confidential information are impregnated with titanium dioxide Confidential information is typed or written on this section. When the document is released for general circulation, a blanket exposure darkens all of the confidential sections.

Non-Impact Printing

Printing can take place through special coatings previously applied to the paper which are UV transparent. An example is pre-varnished paper.

Scratch-off Coating

The principle described above can be exploited with a coating that is opaque to visible light but transparent to UV. A legend or message is written through this coating and the writing is revealed by scratching the opaque coating off.

High Speed Printing Press

The process of the present invention using an

excimer laser is fast, requiring only a 20ns (20 X 10^{-9} seconds) pulse and no drying. The excimer pulses at 250Hz and thus can print at a rate of 250 sheets per second. The short pulse time means that sheets can pass under the laser at a constant speed with no need for a special mechanism to move the exposing mask or make each sheet linger during exposure.

The present invention will be further described with reference to the following Example.

EXAMPLE

A sample of paper loaded with TiO_2 to 32% by weight was exposed to ultraviolet radiation of 248nm wavelengths from a KrF excimer laser. Maximum darkening resulted from an energy density of $3J/cm^2$.

The exposure was made through a metal mask. There was no evidence of degradation of edge definition.

The accompanying Figure is a photomicrograph at 50 times magnification of a sample of the exposed paper. Black particles are evident on and within the fibrous matrix of the paper, but the fibres themselves are unaffected.

CLAIMS:

1. A method of printing onto a cellulosic substrate which contains titanium dioxide, which method comprises irradiating at least a part of the surface of the cellulosic substrate with ultraviolet radiation produced by a laser and having a wavelength of less than 400nm in order to cause the titanium dioxide present in the irradiated area(s) to darken.

2. A method as claimed in claim 1 wherein the laser is an excimer laser.

3. A method as claimed in claim 2 wherein the laser is a krypton fluoride laser with an output at 248nm.

4. A method as claimed in any one of the preceding claims wherein the surface is irradiated with one or more pulses of ultraviolet radiation of a average energy density of $3J/cm^2$.

5. A method as claimed in any one of the preceding claims wherein the cellulosic substrate is paper, card, cardboard, coated paper or a paper covered laminate.

6. A method as claimed in any one of the preceding claims wherein the titanium dioxide is impregnated uniformly throughout the surface of the cellulosic substrate and the substrate is irradiated through a mask.

7. A method as claimed in any one of claims 1 to 5 wherein the titanium dioxide is selectiv ly

impregnated in the surface of the cellulosic substrate and the whole of the substrate surface irradiated.

8. A method as claimed in any one of the preceding claims whenever used for security printing.

9. A method as claimed in claim 7 whenever used for document validation.

10. A method as claimed in any one of claims 1 to 7 whenever used for non-impact printing.

11. A method as claimed in any one of claims 2 to 7 wherein sheets of a cellulosic substrate material impregnated with titanium dioxide are passed beneath the beam of an excimer laser at a rate which correlates with the pulse rate of the laser.

12. A method as claimed in claim 11 wherein the excimer laser pulses at 250Hz and the sheets of the cellulosic material pass beneath the laser beam at a rate of 250 sheets per second.

13. A method as claimed in claim 1 substantially as hereinbefore described with reference to the Example.

Amendments to the claims have been filed as follows

1. A method of printing onto sheets of a cellulosic substrate which contains titanium dioxide, wherein at least a part of the surface of sheets of a cellulosic substrate material impregnated with titanium dioxide are irradiated with ultraviolet radiation produced by an excimer laser and having a wavelength of less than 400nm in order to cause the titanium dioxide present in the irradiated area(s) to darken, the said sheets of the cellulosic material being passed beneath the beam of the laser at a rate which correlates with the pulse rate of the laser.

2. A method as claimed in claim 1 wherein the laser is a krypton fluoride laser with an output at 248nm.

3. A method as claimed claim 1 or claim 2 wherein the surface is irradiated with one or more pulses of ultraviolet radiation of a average energy density of $3J/cm^2$.

4. A method as claimed in any one of the preceding claims wherein the cellulosic substrate is paper, card, cardboard, coated paper or a paper covered laminate.

5. A method as claimed in any one of the preceding claims wherein the titanium dioxide is impregnated uniformly throughout the surface of the cellulosic substrate and the substrate is irradiated through a mask.

6. A method as claimed in any one of claims 1 to

4 wherein the titanium dioxide is selectively impregnated in the surface of the cellulosic substrate and the whole of the substrate surface irradiated.

7. A method as claimed in any one of the preceding claims whenever used for security printing.

8. A method as claimed in claim 6 whenever used for document validation.

9. A method as claimed in any one of claims 1 to 6 whenever used for non-impact printing.

10. A method as claimed in any one of the preceding claims wherein the excimer laser pulses at 250Hz and the sheets of the cellulosic material pass beneath the laser beam at a rate of 250 sheets per second.

11. A method as claimed in claim 1 substantially as hereinbefore described.

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